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IONIC AND NEUTRAL REACTIONS RELEVANT TO COMMUNICATIONS AND IONO--ETC(U)
AUG 77 W L FITE, F KAUFMAN DAAG29-76-G-0342

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A brief review of data on identifying important ions following associative ionization processes of U and Th has indicated that UO_2^+ and ThO_2^+ are probably the respective terminal ions in atmospheric processes. These ions are either formed directly or are produced by the ion-molecule reaction $MO^+ + O_2 \rightarrow MO_2^+ + O$. Two contributions were made to the field of neutral-neutral processes: (1) To aid vibrational relaxation measurements on HX species, a pre-titration flow tube system was built which provides simple and accurate measurements of H-atom densities. (2) A tunable dye laser — next page

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20. Abstract

wavelength narrowing attachment was put into operation which makes possible the measurement of OH densities at $\geq 10^8$ cm^{-3}. This has been used to determine the rate constant of an atmospherically important reaction of the HO_2 radical.

> or = 10 to the 8th power/cu.cm.

IONIC AND NEUTRAL REACTIONS RELEVANT TO COMMUNICATIONS AND IONOSPHERIC PROCESSES

Final Report

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August 15, 1977

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Ionospheric and Neutral Reactions Relevant to Communications and Ionospheric Processes

The portion of this brief program that was addressed to ion chemistry was concerned with ions that can be formed by thermal energy associative ionization reactions between groundstate debris atoms and atmospheric species. Such ions are energetically forbidden from dissociative recombination with electrons, and hence the electrons formed in these reactions would be expected to be long lived, which in turn would affect communications over long term periods.

The question under study was whether or not these primary ions, although themselves unable to dissociatively recombine, might undergo ion-molecule reactions with the atmospheric species to produce secondary ions that are able to recombine with electrons. If this is the case, then the electrons originaly produced might not be so long lived.

It was known at the onset of this study that in two cases such ion-molecule reactions can proceed. The first was $UO_2^+ + O_2 \rightarrow UO_3^+ + O$; however this reaction requires that the UO_2^+ be very highly excited, a situation which occurs if the UO_2^+ is formed by associative ionization. When the UO_2^+ is in or near the groundstate, however, as it can be made by surface ionization or after radiating from a highly excited level the reaction does not occur.

The second case is the reaction $UO_2^+ + NO_2 \rightarrow UO_3 + NO^+$. In this case, the reaction proceeds irrespective of the manner of formation of the UO_2^+ and indicates that the reaction even with groundstate species is exoergic. This finding is particularly troublesome in view of the believed values of the binding energies and ionization potentials of

the relevant species. The finding appears to indicate that errors of at least 0.4 eV exist in the accepted energetics of the uranium-oxygen system.

Because of the very small effort available under the present study, the activity consisted primarily of a review of data taken previously with regard to the matter of ion-molecule reactions involving ions formable via associative ionization. A secondary activity was a more thorough analysis of an experiment on the ion-molecule reaction $UO^+ + O_2 \rightarrow UO_2^+ + O$,[1] which was in progress concurrently with the presently described efforts, than would otherwise have been made.

A review of existing data on uranium indicated that UO_2^+ seems to be the terminal ion of importance for upper atmospheric considerations. This ion can be formed directly by reaction with O_2, and the UO^+ ion formed by reaction with O atoms can react with ambient N_2O and O_2 to form UO_2^+ with a reaction rate coefficient of about 2×10^{-9} cm^3/sec. Reaction with O_3 [2] yields UO^+ and UO_2^+ and again the UO^+ can be converted to UO_2^+ by reaction with O_2.

Similarity of associative ionization data on thorium to that on uranium suggests that the same pattern holds here. The only difference is that in reaction with ozone, the ThO_3^+ ion is formed (at a level of about 10^{-3} times the ThO^+ production). It is believed that the ThO_3^+ can dissociatively recombine, although we have not been able to find the relevant thermodynamic data in the literature.

With regard to ion-molecule reactions, we were not able to find any atmospheric species with which groundstate UO_2^+ can react to form an ion which can dissociatively recombine except NO_2. Here again, the relevant energetics are not complete, however, and as noted above, we believe that even the energetics of the uranium-oxygen system are in error.

It would appear at this point that it is only NO_2 that can lead through ion molecule reactions with UO_2^+, after it has had time to radiate out of the highly excited states in which it is formed, to give reduction of the lifetime of electrons formed initially by associative ionization.

In the part of this small program which was devoted to the study of neutral reactions of ionospheric importance, contributions to two research areas were made. The first one deals with infrared chemiluminescence measurements in studies of vibrational energy transfer of excited air species and the second one deals with tunable dye laser detection of radical species in a discharge-flow system where neutral-neutral reaction rate constants are measured.

(1) The work on vibrational relaxation of highly excited diatomics such as HCl, HF, OH is carried out in a discharge-flow system with very fast pumping ($\leq$ 100 m s^{-1}) and modualted generation of H-atoms as precursors of the desired species by chemical reaction, e.g. $H + ICl \rightarrow HCl^{\ddagger} + I$ or $H + O_3 \rightarrow OH^{\ddagger} + O_2$. Sensitive detection of IR radiation by cooled InSb detectors and spectral resolution by cooled circularly variable filters enables us to characterize the vibrationally excited products, then to perturb that distribution by adding quencher molecules and to analyze the overall relaxation process in terms of the V-V transfer rates brought about by collisions with the quencher.

The contribution of the present grant to this important study was the design, building, and testing of a pre-titration system upstream of the main flow tube in which the H-atom density can be measured accurately at levels in the 10^{11} to 10^{13} cm^{-3} range. This involves the measured addition of NO_2 or ClNO titrant in a smaller upstream flow tube which carries all of the H-atom flow from the microwave discharge

but only 1 to 10% of the total He diluent. The local H-atom concentration is therefore 10 to 100 times greater than in the main flow tube and the local flow velocity is smaller. The pre-titration therefore goes quickly to completion. The endpoint is detected by the IR measurement in the chemiluminescence cell in the main flow tube where ICl or ClNO is added just upstream of the cell. The method thereby represents a simple and accurate in-situ measurement of [H] which requires neither additional equipment nor time-consuming procedures which may interrupt the normal course of the experiments. It has worked extremely well ever since its inception and development.

(2) A considerable fraction of the funds available to the neutral reaction portion of this small grant were used to purchase the wavelength narrowing attachment for our tunable dye laser (Chromatix Model CMX-4). This accessory which consists of 4 Fabry-Perot etalons, reduces the laser bandwidth from about 3 to 0.15 cm^{-1} in the visible near 600 nm and from about 6 to 0.3 cm^{-1} after frequency doubling in the u.v. Through the use of both the doubling and narrowing options we were able to detect OH radicals in the discharge flow reaction system at very high sensitivity, i.e. 1×10^8 cm^{-3} concentration. The laser is pulsed at about 10 Hz and the OH fluorescence signal is processed using a boxcar integrator whose time gate is set so that it sums the OH emission for several microseconds beginning about 1 μs after the peak of each laser pulse. This ultra-sensitive detection of OH is used in conjunction with the simultaneous detection of H and O by vacuum u.v. resonance fluorescence at 121.5 and 130.2 nm to measure the rates of some HO_2 radical reactions. HO_2 is generated by the recombination reaction $H + O_2 + M \rightarrow HO_2 + M$ which is made to go to completion inside a coaxial

injector tube within our flow tube so that neither H nor OH are present when HO_2 is released into the main flow tube. It is then mixed with other reactant such as NO with which it reacts to form NO_2 and OH which is detected by laser fluorescence. Initial data on this atmospherically important reaction show it to be much faster than indicated in earlier studies[3,4] by other workers, i.e. its rate constant is near 1×10^{-11} $cm^3\ s^{-1}$ rather than the values of 0.4 to 1×10^{-12} which had been reported by more indirect means.

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